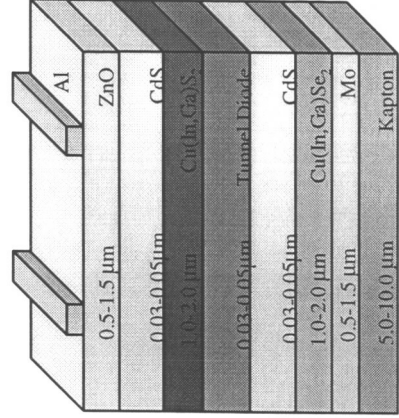
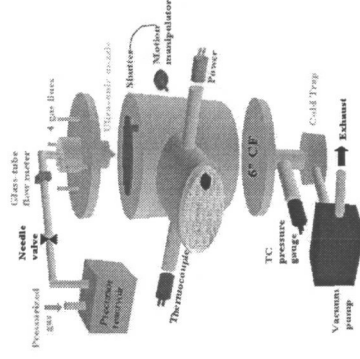
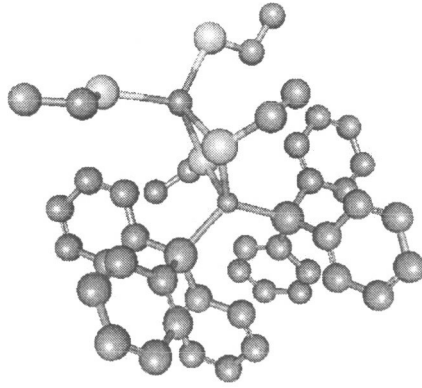


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# Development of Thin Film Solar Cells for Space Applications at NASA Glenn Research Center

Dr. John E. Dickman  
Dr. Aloysius F. Hepp  
Dr. Kulbinder K. Banger  
Dr. Jerry D. Harris  
Dr. Michael H. Jin



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## **ABSTRACT**

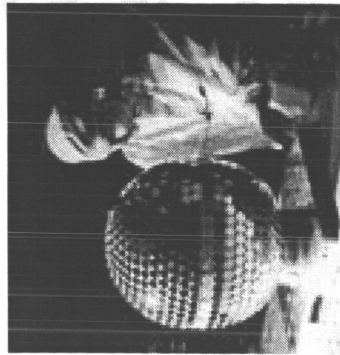
NASA GRC Thin Film Solar Cell program is developing solar cell technologies for space applications which address two critical metrics: higher specific power (power per unit mass) and lower launch stowed volume. To be considered for space applications, an array using thin film solar cells must offer significantly higher specific power while reducing stowed volume compared to the present technologies being flown on space missions, namely crystalline solar cells.

The NASA GRC program is developing single-source precursors and the requisite deposition hardware to grow high-efficiency, thin-film solar cells on polymer substrates at low deposition temperatures. Using low deposition temperatures enables the thin film solar cells to be grown on a variety of polymer substrates, many of which would not survive the high temperature processing currently used to fabricate thin film solar cells. The talk will present the latest results of this research program.

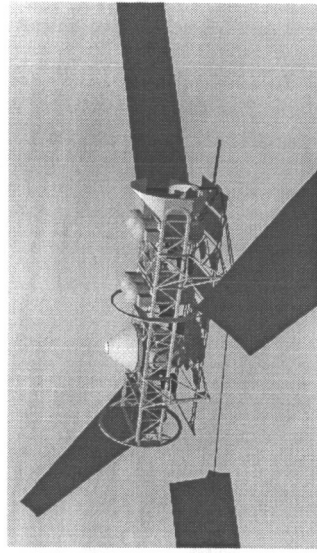
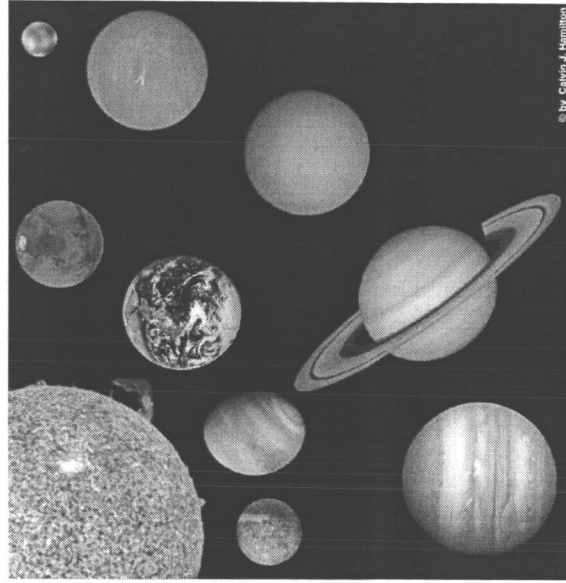


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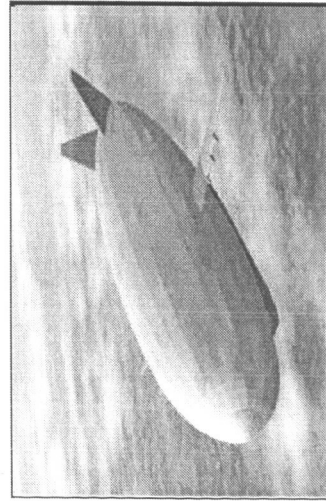
# Missions for Thin Film Technology



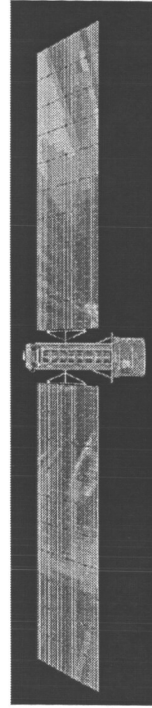
(Nano-)Satellite Power



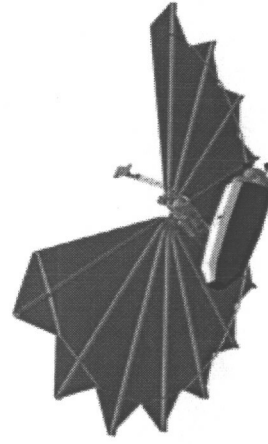
Planetary Surface Power



Ultra-Large Airships



Space Solar Power



Solar Electric Propulsion

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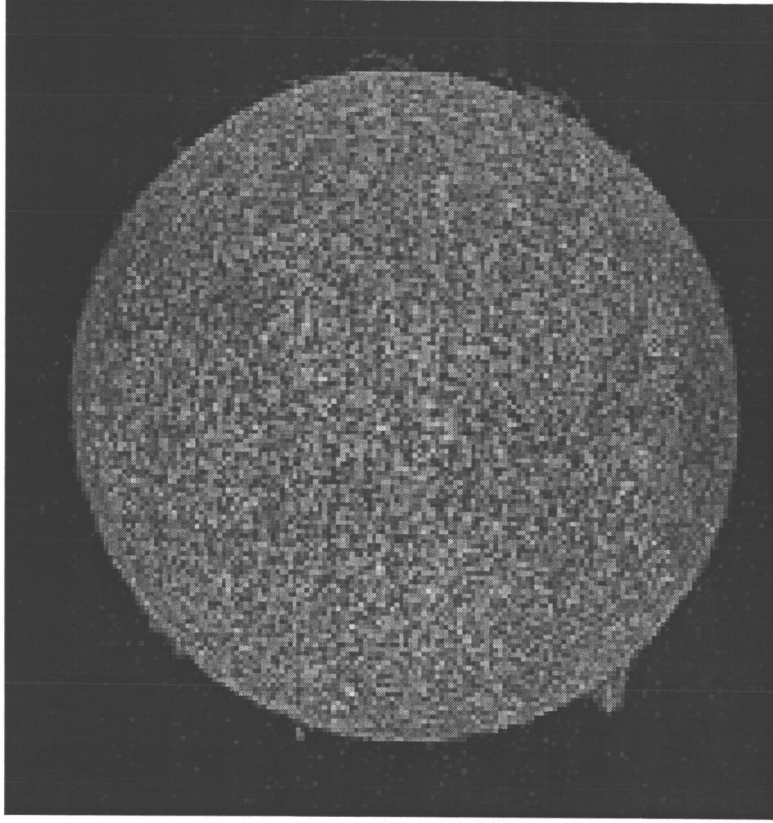
## Why CIS & CISE Thin Films?

### Radiation tolerant

CIS, CISE solar cells are among  
the most radiation tolerant cells.

### High efficiency

The record CISE solar cell  
has an efficiency of 18.8%.



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# Objectives: Key TF Array Issues

- **Thin-film cell efficiencies increase and/or substrate mass decreases**
  - Need economical large-scale production of large-area ( $>10\text{-cm}^2$ ) thin-film cells with stable efficiencies  $\sim 10\%$  to  $15\%$  (1-Sun AM0) on low-mass substrates (1-mil metallic, 5-mil composite, 2-mil polymer):

**LTCVD offers opportunity to employ polymer substrates**

- **Thin-film solar arrays are designed and space qualified**
  - Need packaging, deployment systems and support structures tailored to thin-films:

**Work in partnership with Array TPA to produce  
new structural and support technologies**

- **Thermal issues identified as major impediment to good EOL efficiency**
  - TF array benefits should not be mitigated by spacecraft-level operations issues associated with larger area, low-mass devices:

**Develop new device structures (Back/front), new (clear) substrates (CP-1),  
and high emissivity coatings (conducting oxide films - e.g.  $\text{WO}_3$  or  $\text{MoO}_3$ )**

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# Thin Film Technology Road Map

## NASA GRC Space Power Technology Road Map

| Technology Focus Area  | 2002 – 2005<br>Establish a Presence  | 2006 – 2010<br>Expand Our Horizons  | 2011 – 2023<br>Develop the Frontiers  |
|--|--|---|---|
| <b>Thin-Film Solar Cells</b><br>Provide advanced thin-film technologies for challenging environments and applications. Innovative chemical concepts and processing will enable use of polymer substrates. This technology is enabling for very large inflatable arrays and numerous aerospace exploration missions such as: direct-drive electric propulsion, high-altitude airships, and space solar power. | <ul style="list-style-type: none"> <li>• <b>Demonstrate</b><br/>AM0 cell efficiency &gt;8% on lightweight substrates using single-source precursor, low-temperature deposition process on polymers.</li> <li>• <b>Integrate</b><br/>thin-film technology and lightweight array design.</li> <li>• <b>Investigate</b><br/>high-emissivity coatings for high-voltage array operation.</li> </ul> | <ul style="list-style-type: none"> <li>• <b>Demonstrate</b><br/>dual-junction thin-film cells on lightweight substrates.</li> <li>• <b>Develop</b><br/>monolithic interconnection technologies for thin-film cells.</li> <li>• <b>Demonstrate</b><br/>dual-junction cell with AM0 cell efficiency &gt;20%.</li> </ul> | <ul style="list-style-type: none"> <li>• <b>Develop</b><br/>multi-junction thin-film cells on lightweight structures with efficiencies &gt;20%.</li> <li>• <b>Demonstrate</b><br/>array operation at high-voltages (&gt;1000V) with high-emissivities.</li> </ul> |

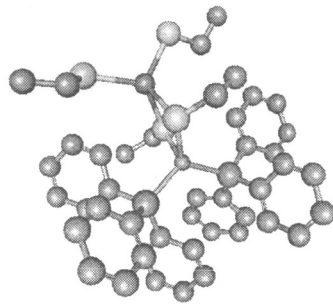
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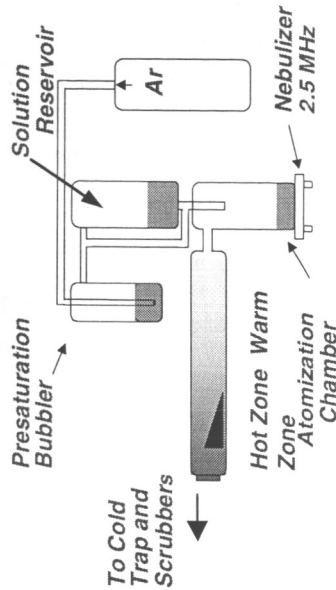
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# Overview of Technical Approach

- Low-temperature processing with Single-Source Precursors

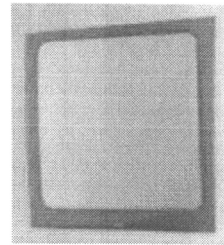


Single-source  
precursor

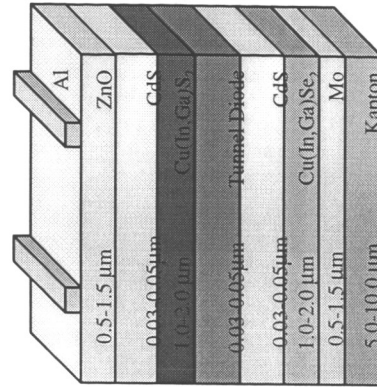


Horizontal Chemical  
Spray Pyrolysis or CVD Reactor

- Advanced materials (substrates) and novel devices (multi-junction)



Mo on polymer  
substrate



Multi-junction  
thin film device

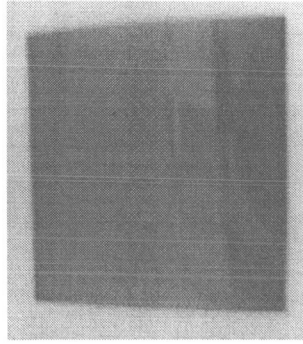
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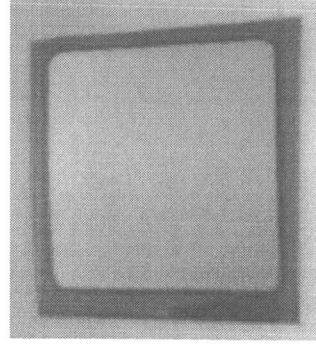
# Polymer Substrates Require Low Processing Temperatures

**Kapton™**



A thin-film space qualified flexible polymer substrate

1 $\mu$ m molybdenum deposited by rf sputtering



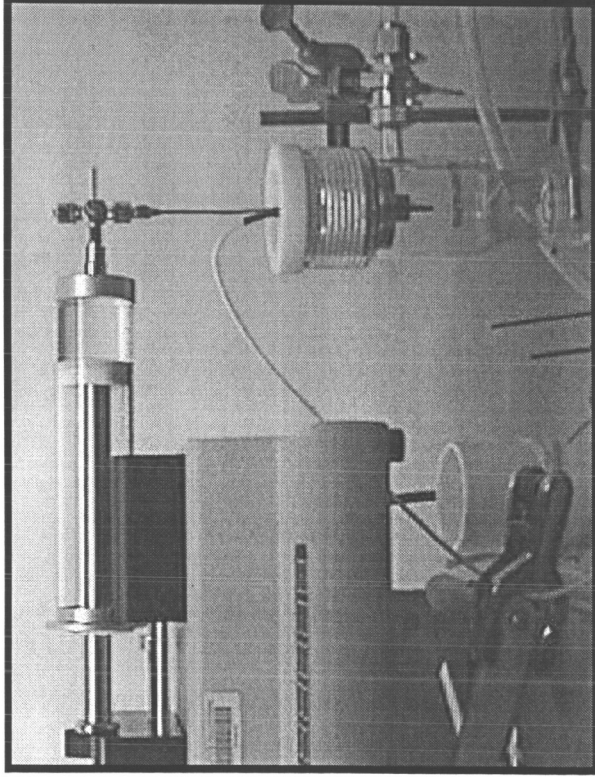
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# **CuInS<sub>2</sub> Thin Film Deposited with Liquid Single-Source Precursor**

- Method: Spray pyrolysis under Ar-flow (vertical cold-wall reactor), Commercial ultrasonic spray nozzle (freq: 120 kHz)
- Substrate temperature: 400 °C
- Precursor: Liquid phase single-source, [ $\{P(n-Bu)_3\}_2Cu(SEt)_2In(SEt)_2\}$ ]  
(Decomposition temperature: ~ 260 °C)



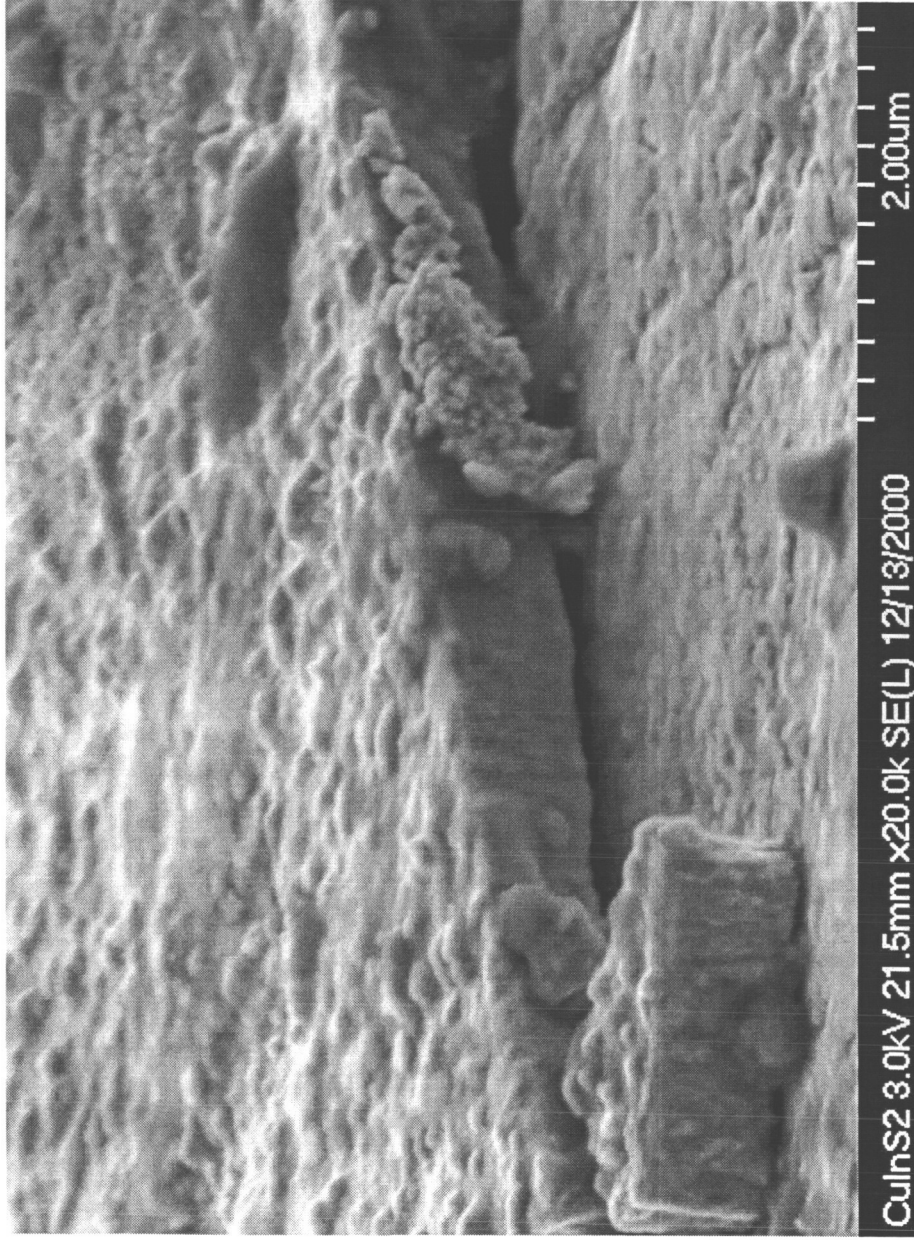
- No need to control the height of the liquid column (reliable droplet size distribution)
- No deposits at the wall and better transport of sprays (better yield)
- Easy to model aerosol dynamics to explore the process parameters

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# SEM of Surface of $\text{CuInS}_2$ Thin Film on Mo



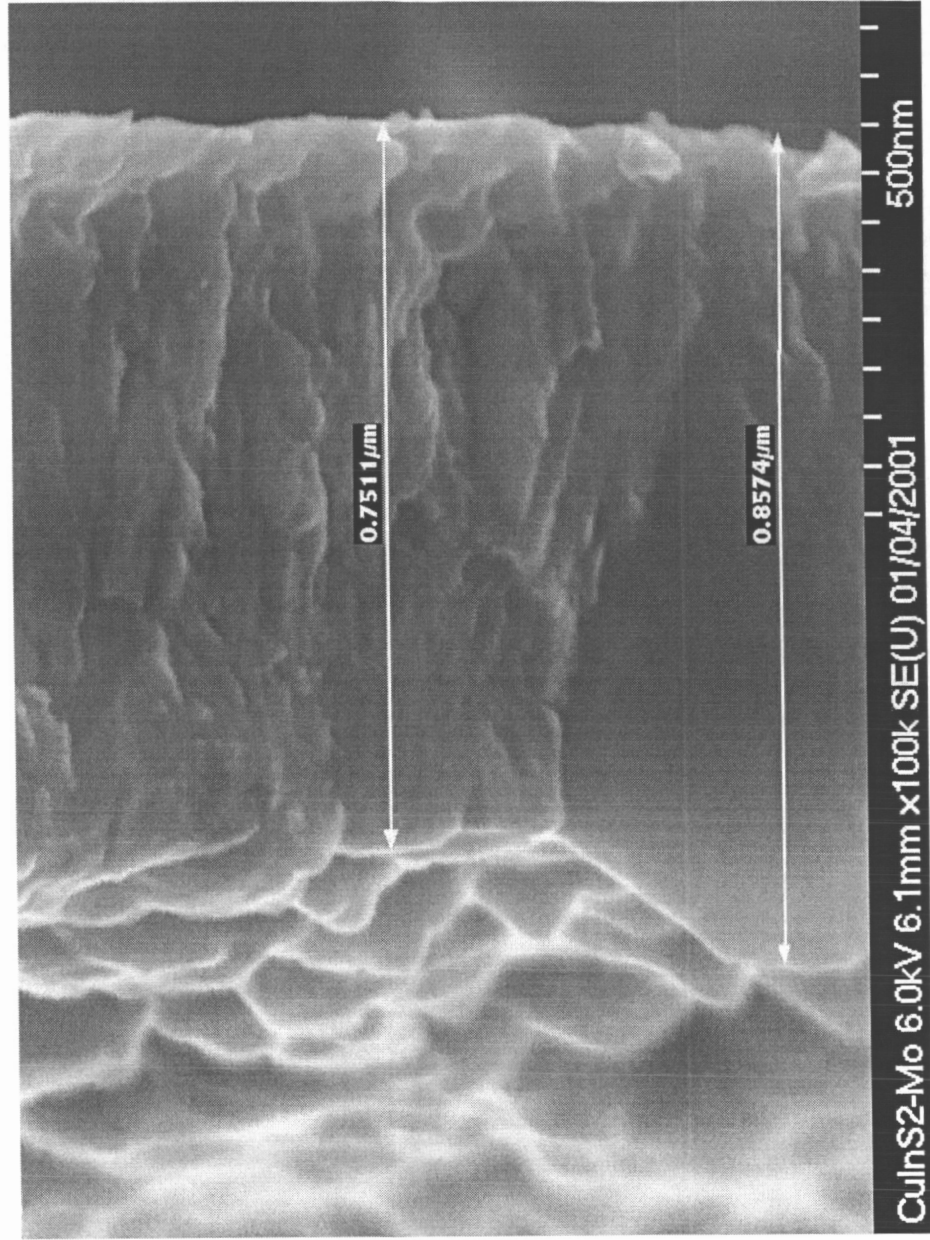
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# SEM of Edge View of $\text{CuInS}_2$ Thin Film on Mo



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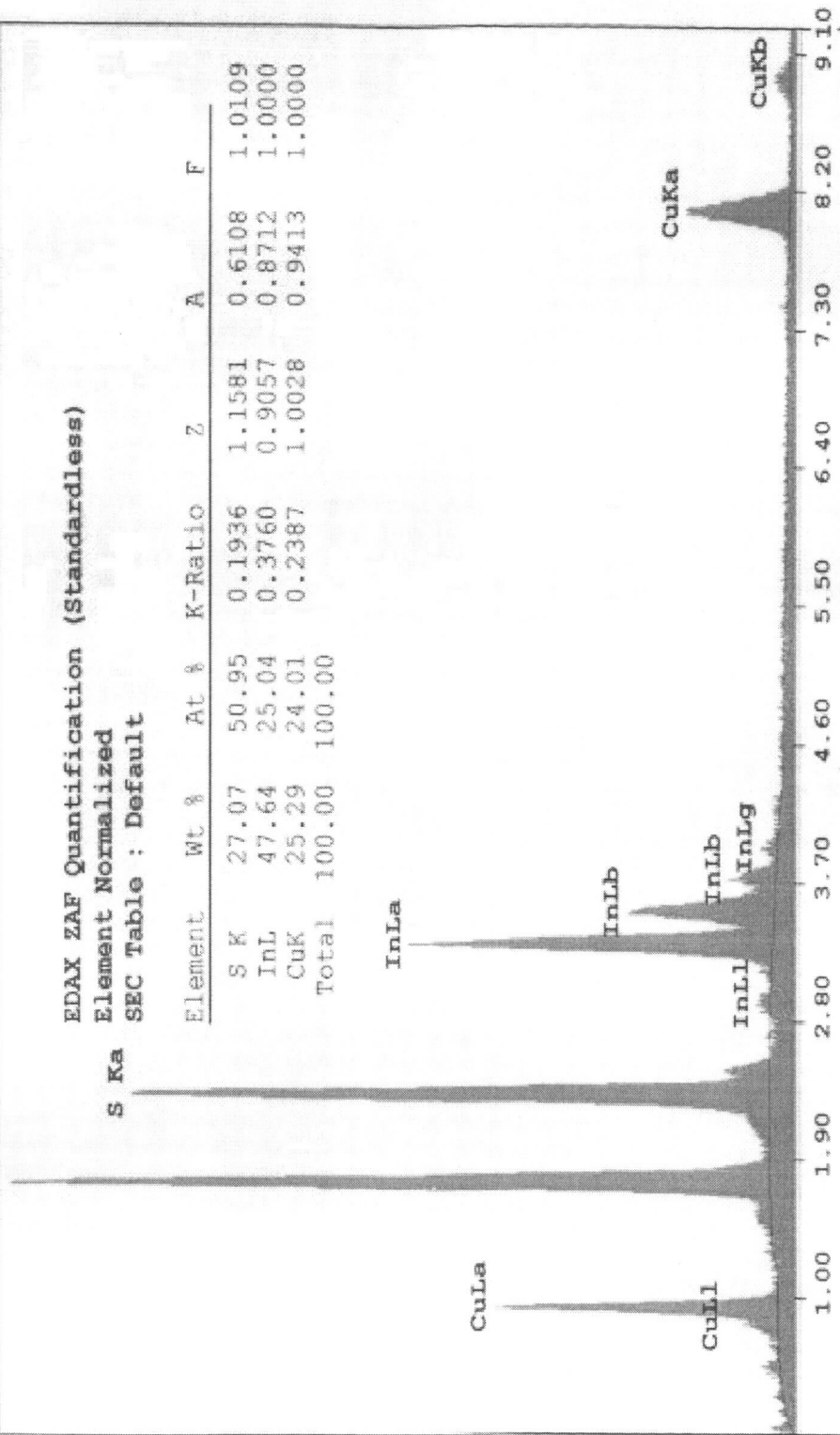
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# EDS Spectrum for $\text{ClS}_2$

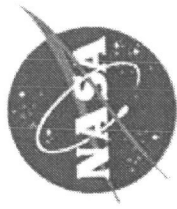
kV:20.0 Tilt:0.0 Take-off:21.7 Det Type:SUTW+ Res:129 Tc:35

FS : 2546 Lsec : 206

1-Dec-2000 10:36:18



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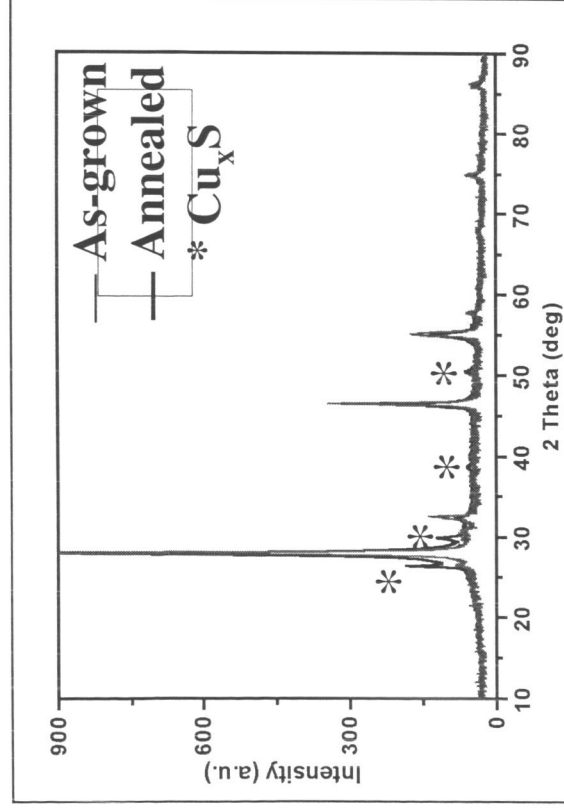


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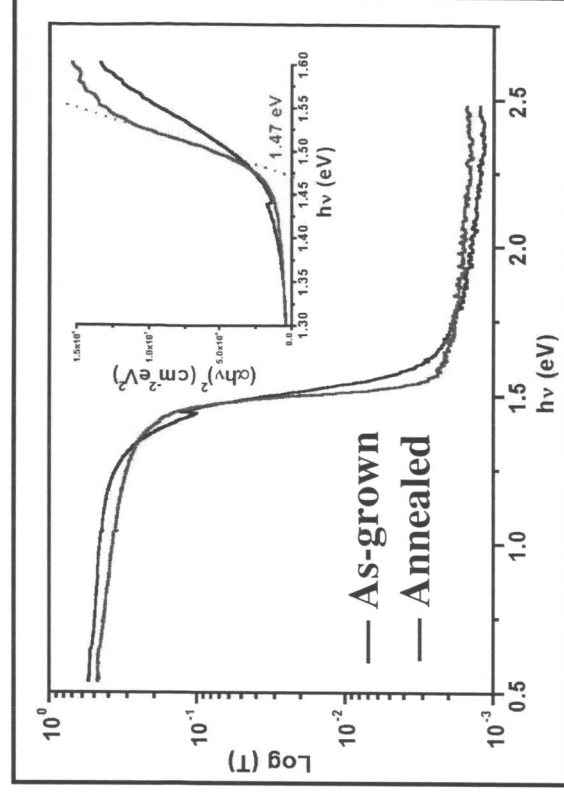
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# CuInS<sub>2</sub> Thin Film Deposited with Liquid Single-Source Precursor

X-ray diffraction and optical analysis

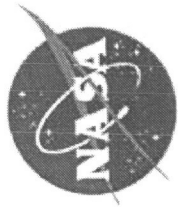


- Chalcopyrite-CuInS<sub>2</sub> confirmed with XRD and EDS.
- Volatile secondary phase can be easily removed by annealing.



- Band gap : ~ 1.47 eV after post-thermal treatment.
- Improved band-edge absorption after annealing.

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# **CuInS<sub>2</sub> Thin Film Deposited with Liquid Single-Source Precursor**

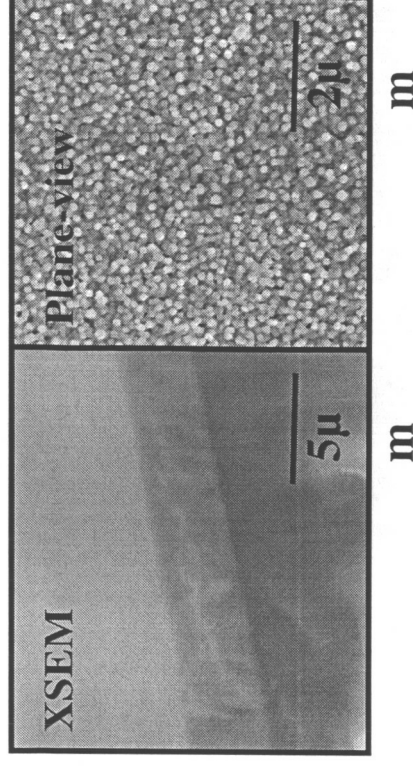
## **Tencor profiler (Roughness)**

RMS deviation: ~ 200 nm  
(well agreed with grain size)

- Better yield: Growth rate > 3 Å/s
- Grain size : ~ 200 nm

## **4 point probe measurement (Resistivity)**

3~20 Ω-cm (before annealing)  
1~5 Ω-cm (after annealing)



**Best conductivity among films grown with same family  
of single-source precursors synthesized at GRC**

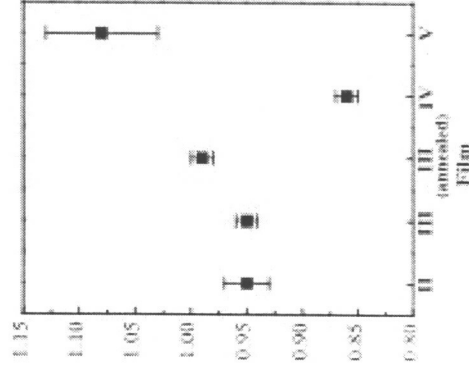
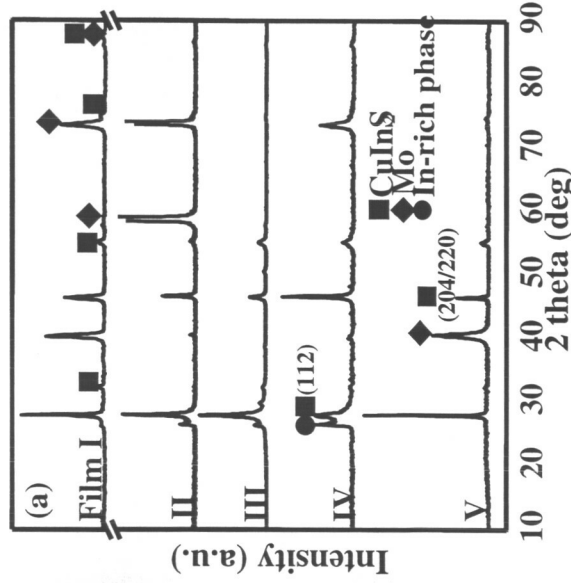
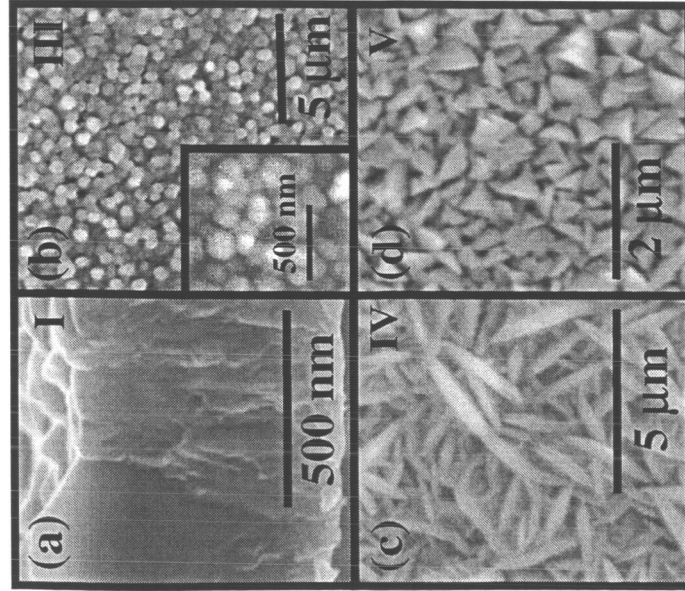
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# Texture and Composition of $\text{CuInS}_2$ Films by AACVD Using Single-Source Precursors



- ❖ **(112)-Oriented films**
  - ❖ Without secondary phase
  - ❖ Slightly Cu-rich
- ❖ **(204/220)-Oriented films**
  - ❖ In-rich
  - ❖ Always included secondary phase
- ❖ **Cu/In ratio increased by removing the secondary phase**
  - ❖ Post-growth annealing at 600 °C
- ❖ **Single-phase chalcopyrite  $\text{CuInS}_2$  films with a dense columnar grain structure** were obtained
  - ❖ Depositing (112)-oriented films
  - ❖ Grain size was small ( $\leq 0.5 \mu\text{m}$ )
    - ❖ Due to the absence of a quasi-liquid Cu binary phase
- ❖ **Further development necessary to grow films with higher [Cu] to obtain bigger grains suitable for solar cells**

A - (A (s) @ 400°C; 760 torr)  
B - (B (l) @ 400°C; 760 torr)  
C, D - (C (l) @ 400°C; 10 torr)  
Dense, faceted grains: A & D  
(Increased flow rate C to D)

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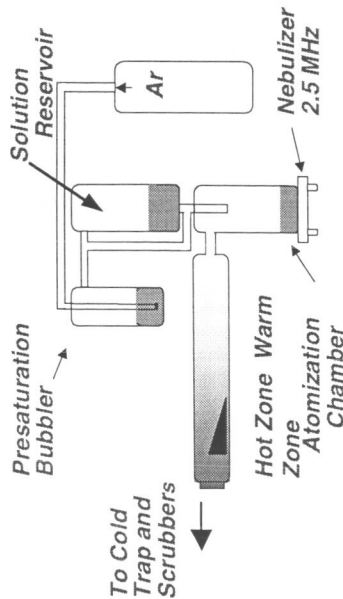


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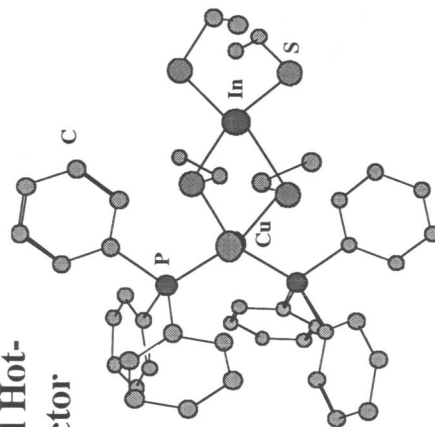
# Low-Temperature Spray CVD Process for $\text{CuInS}_2$ Uses Single-Source Precursors

Analytical Data for Series of Single-Source Precursors

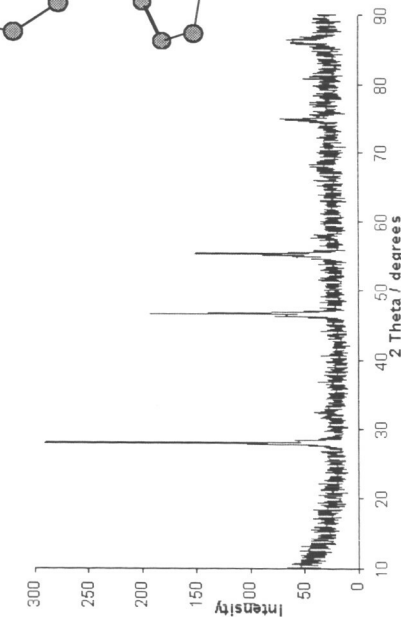
| CIS/CISe Derivative   | TGA               |           | DSC     |                |
|---|-------------------|-----------|---------|----------------|
|   | T°C@max<br>% loss | % Residue | M.P. °C | Decomp.<br>T°C |
| $[(\text{PPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$            | 269               | 25        | 122     | 239, 266       |
| $[(\text{AsPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$           | 233               | 18        | 47      | 204, 276       |
| $[(\text{SbPh}_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$           | 239               | 26        | 45      | 231, 271       |
| $[(\text{P}(n\text{-Bu})_3)_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$ | 186               | 27        | -       | 233, 269       |
| $[(\text{PPh}_3)_2\text{Cu}(\text{Si-Pr})_2\text{In}(\text{Si-Pr})_2]$        | 254               | 29        | 163     | 260            |
| $[(\text{PPh}_3)_2\text{Cu}(\text{SPh})_2\text{In}(\text{SPh})_2]$            | 325               | 22        | 117     | 170, 280       |
| $[(\text{PPh}_3)_2\text{Cu}(\text{SePh})_2\text{In}(\text{SePh})_2]$          | 253               | 27        | 53      | 176, 219       |



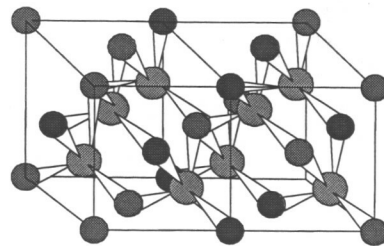
Schematic of Horizontal Hot-Wall Spray CVD reactor



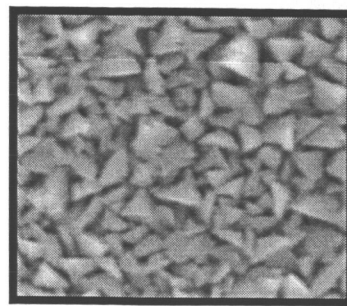
Ball and Stick Schematic of Single-Source Precursor Synthesis of  $\text{CuInS}_2$



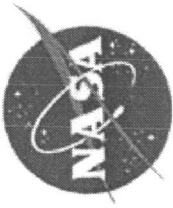
XRD Pattern of Single-Phase  $\text{CuInS}_2$   
Produced from Liquid Single-Source Precursor



SEM of Dense Faceted  $\text{CuInS}_2$  CVD-Produced at 400°C (0.2  $\mu\text{m}$  grains)



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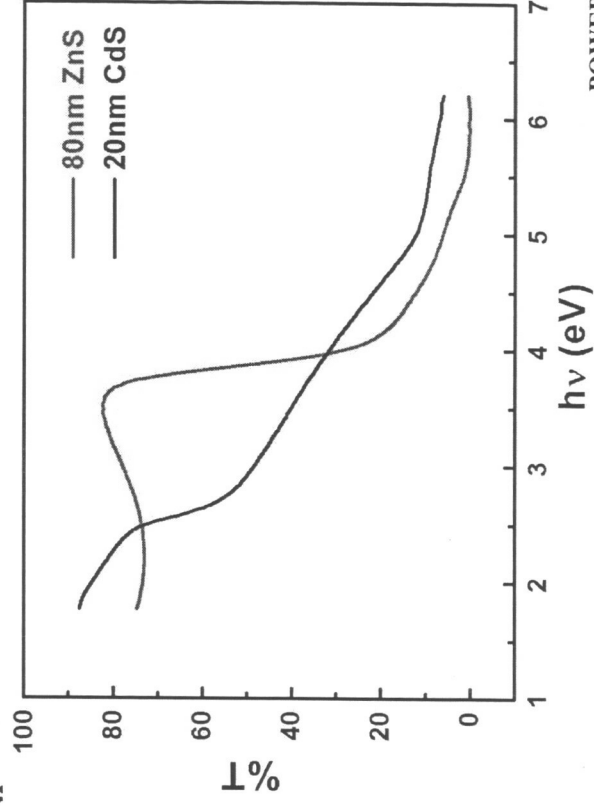
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# Interface Engineering

- Alternatives to CdS
  - (Cd,Zn)S : Band gap ( $2.5 \sim 3.5$  eV),  $\Delta E_c$  ( $-0.45$  to  $0.5$  eV).
  - Interface engineering: Cd or Zn solution treatment (n-type doping) followed by CdS deposition.
- Advantages of chemical bath deposition over PVD
  - Simple, easy, less damage, and conformal deposition.
  - Removal of the native oxide on the  $\text{CuInS}_2$  surface re-establishing positively charged surface states for natural n-type inversion.
  - Doping effect from Cd ions.

• CdS and ZnS thin films deposited using non-toxic complexing agents (tri-sodium citrate and ammonia)  
\* hydrazine hydrate is commonly used.

- Barrier : single phase formation instead of solid solution.



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Michael Jin - OAI

M. Smith - OAI

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Ryne Raffaele - RIT (FL Tech)

John Scofield - Oberlin

Bill Buhro - WUStL

Andy Barron - Rice Univ.

Mercouri Kanatzidis - MSU

### Students

Jonathan Cowen - CSU (CWRU)

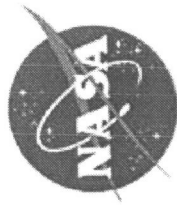
Tony Sutorik - MSU

Jen Hollingsworth - WUStL

Eva Lau - SUNYA (OAI)

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# Conclusions:

## Thin Film Technology Issues

### Thin-Film Arrays will be used in space WHEN...

- Thin-film cell efficiencies increase and/or substrate mass decreases
  - ✓ Need economical large-scale production of large-area ( $>10\text{-cm}^2$ ) thin-film cells with stable efficiencies  $> 10\%$  to  $15\%$  (1-Sun AM0) on low-mass substrates (1-mil metallic, 5-mil composite, 2-mil polymer)
- Thin-film cell space qualification is completed
  - ✓ Need to demonstrate tolerance to radiation, thermal cycling (delamination), mechanical strain (packaging and blanket tensioning) and (for amorphous silicon) light-induced instability
- Thin-film solar arrays are designed and space qualified
  - ✓ Need packaging, deployment systems and support structures tailored to thin-films
- Appropriate missions are identified...
  - ✓ ...that would benefit from thin-film array attributes (high specific power, good package-ability, radiation tolerant, low cost – e.g. Solar Electric Propulsion missions)
  - ✓ ...whose benefits are not mitigated by spacecraft-level operations issues associated with larger area, low-mass arrays

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